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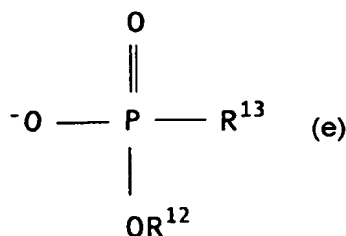
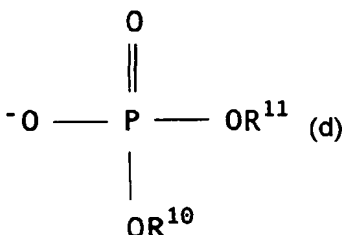
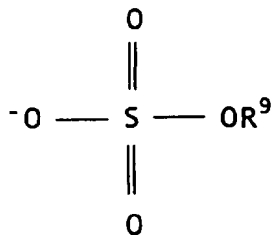
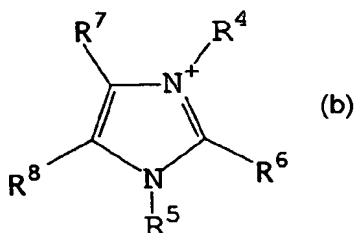
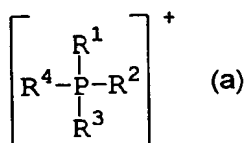
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(54) Title: PHOSPHONIUM AND IMIDAZOLIUM SALTS AND METHODS OF THEIR PREPARATION



(57) Abstract: Novel phosphonium and imidazolium salts and methods for preparing them are disclosed. The novel phosphonium and imidazolium compounds are useful as polar solvents and have the general formula (I): Q^+X^- wherein Q^+ is formula (a) or formula (b); and X^- is formula (c), formula (d) or formula (e); and wherein: each of R^1 , R^2 , R^3 , R^4 , R^5 , R^9 , R^{10} , R^{11} , R^{12} , and R^{13} is independently a hydrocarbyl group; each of R^6 , R^7 , and R^8 is independently a hydrogen or hydrocarbyl group.



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TITLE: PHOSPHONIUM AND IMIDAZOLIUM SALTS AND METHODS OF THEIR
PREPARATION

FIELD OF THE INVENTION:

The present invention relates to novel phosphonium
5 and imidazolium salts, their methods of preparation and their
use, for example, as polar solvents.

BACKGROUND OF THE INVENTION:

Low melting or liquid phosphonium and imidazolium
salts have found utility as polar solvents known as "ionic
10 liquids". Ionic liquids provide an attractive alternative to
traditional organic solvents for chemical reactions for many
reasons. Ionics liquids display low vapour pressure which, for
industrial purposes, is a very important feature. They are
essentially non-volatile, a property that eliminates many of
15 the containment problems typically encountered with traditional
organic solvents. Since ionic liquids are often composed of
poorly coordinating ions, they have the potential to provide a
highly polar yet poorly coordinating solvent. Moreover, many
of these solvents are immiscible with traditional organic
20 solvents and therefore provide a non-aqueous polar alternative
for use in two-phase systems. Because of their distinctive
solvent characteristics, they can be used to bring unusual
combinations of reagents into the same phase. A recent review
of the properties and uses of ionic liquids is provided in an
25 article entitled "Room-Temperature Ionic Liquids. Solvents for
Synthesis and Catalysis," by Thomas Welton (Chem. Rev. 1999,
99, 2071-2083).

Ionic liquids provide solvents with a wide liquid
range and a high degree of thermal stability. However, there
30 remains a need for increasing the solvent options available to

chemists by developing novel ionic liquids with distinctive physical and chemical properties.

Ionic liquids can be prepared by a two step process, comprising the steps of (a) reacting a nitrogen-containing compound (for example, imidazole) or a phosphorus-containing compound with an alkylhalide to obtain a quaternary nitrogen or phosphorus halide salt; and (b) exchanging the halide ion with a suitable anion (ion exchange or metathesis) to obtain a low-melting quaternary nitrogen or phosphorus salt. This process has several drawbacks. For example, the end-product can be contaminated with residual halide ion, which may interfere with the activity of halide-sensitive catalysts. For instance, halide ions such as chloride ions coordinate with group VII metals such as palladium and platinum. If an ionic liquid is to be used in an environment where halide ions are unacceptable, even at low levels, halide salts should not be used in the starting materials or a further process must be used which ensures removal of halide ions from the ionic liquid. Also, the two-step process is inconvenient, as the ion-exchange step produces salt or acid side-products that must be removed by washing with water.

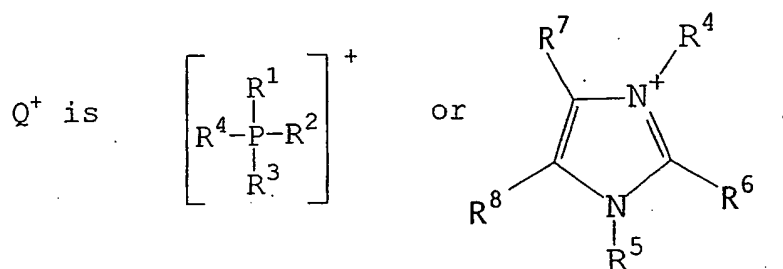
SUMMARY OF THE INVENTION:

The current invention provides novel ionic compounds that find utility as ionic liquids and methods of preparing these compounds. The novel ionic compounds can have a broad range of phosphonium or imidazolium cations and a broad range of sulfate, phosphate or phosphonate anions

Thus, the current invention provides:

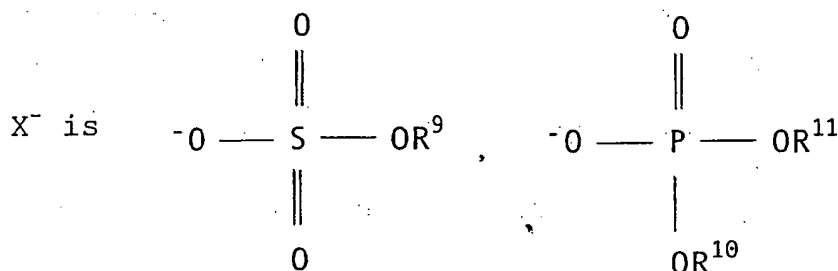
(1) a compound having the general formula (I):

wherein



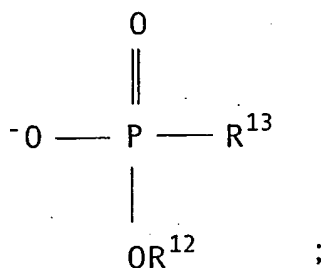
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and



10

or



and wherein:

each of R^1 , R^2 , R^3 , R^4 , R^5 , R^9 , R^{10} , R^{11} , R^{12} , and R^{13} is
 15 independently a hydrocarbyl group;

each of R^6 , R^7 , and R^8 is independently a hydrogen or hydrocarbyl group;

with the provisoes that:

(i) when Q^+ is a phosphonium cation and X^- is a
 20 phosphate, or a phosphonate anion other than a phosphonate in which R^{13} is perfluorohydrocarbyl, then R^1 , R^2 , R^3 , and R^4 each has three or more carbon atoms;

(ii) when Q^+ is a phosphonium cation and X^- is a sulfate then the sum of carbon atoms in R^1 , R^2 , R^3 , and R^4 is greater than 4;

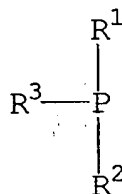
5 (iii) when Q^+ is an imidazolium cation, X^- is not a sulfate anion; and

(iv) when Q^+ is a phosphonium cation, X^- is methylsulfate, and one of R^1 , R^2 , R^3 and R^4 is methyl, the other of R^1 , R^2 , R^3 and R^4 cannot all be 2-cyanoethyl.

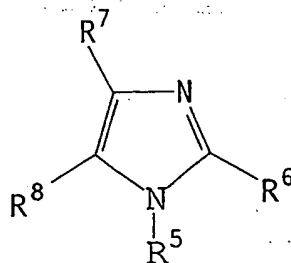
10 In another aspect, the invention provides:

(1) a process for preparing a compound of formula (I), as defined above, wherein:

(a) a compound of formula (II):

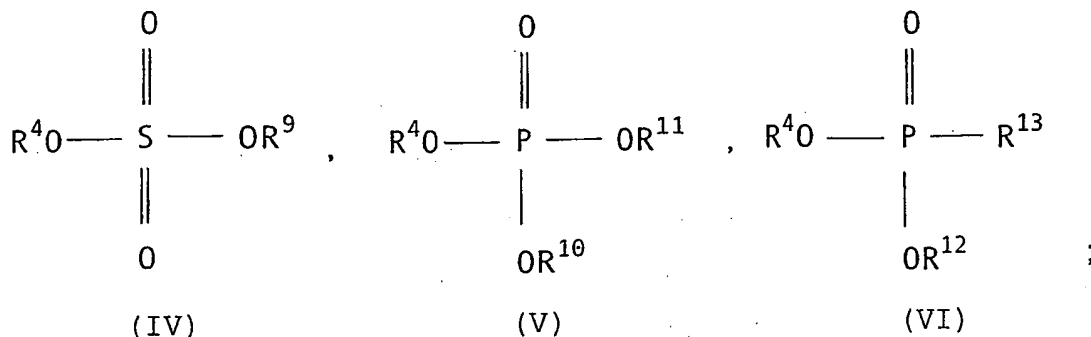


15 wherein each of R^1 , R^2 , and R^3 is defined as above, or formula (III):



20 wherein each of R^5 , R^6 , R^7 and R^8 is defined as above, is reacted with:

(b) a compound defined by one of the following formulae:



wherein each of R^4 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} is defined as above.

DESCRIPTION OF PREFERRED EMBODIMENTS:

Suitable hydrocarbyl groups for R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} include: C_1 - C_{30} alkyl, C_3 - C_8 cycloalkyl, C_2 - C_{30} alkenyl, C_2 - C_{30} alkynyl, C_6 - C_{18} aryl, or C_7 - C_{30} aralkyl, although hydrocarbyl groups with not more than 20 carbon atoms are preferred. It is noted that R^{13} can also be a perfluoroalkyl group. It is possible for the groups R^1 to R^{12} , and R^{13} when not perfluoroalkyl, to bear substituents, or to include heteroatoms, provided that the substituents or heteroatoms do not interfere with the preparation of the compounds of the invention, and do not adversely affect the desired properties of the compound. Acceptable substituents may include alkoxy, alkylthio, halo, carboxy, amino, acetyl, and hydroxyl groups, and heteroatoms that may be acceptable include nitrogen, oxygen and sulphur. Substituents are likely to increase the cost of the compounds of the invention and as the compounds are often used as solvents, they are used in such volume that cost is a significant factor. Hence, it is contemplated that, for the most part, substituents will not be present, although compounds in which R^{13} is perfluorinated hydrocarbyl constitute a preferred embodiment. If necessary, one of skill in the art can readily determine whether substituents or heteroatoms of the hydrocarbyl groups interfere with preparation or desired properties of the compounds by

routine experimentation that does not involve the exercise of any inventive faculty.

Preferred values for R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} include alkyl groups of 1 to 20 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, n-pentyl, cyclopentyl, isopentyl, n-hexyl, cyclohexyl, (2,4,4'-trimethyl)pentyl, cyclooctyl, tetradecyl, etc. Alkyl groups of 3 to 10 carbon atoms are especially preferred values for R^1 to R^{13} .

10 For compounds containing a phosphonium cation, it is desired in some cases that R^1 to R^4 shall not be identical and preferably, that at least one of R^1 to R^4 shall contain a significantly higher number of carbon atoms than the others of R^1 to R^4 . Phosphonium cations in which R^1 to R^4 are not
15 identical are referred to as "asymmetric".

In some cases, it is preferred that at least one of R^1 to R^{13} contains a higher number of carbon atoms, for example 14 or more. For example, the presence of one or more long alkyl chains may increase the ability of a phosphonium or imidazolium
20 salt to dissolve nonpolar organic compounds.

In general, it is preferred that the salt of the current invention is a liquid below 100°C, more preferably below 50°C, and most preferably at or below room temperature. Preferred compounds, therefore, are those in which the
25 particular groups R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} , are selected to yield compounds that are liquid at room temperature. In general, increasing the total number of carbon atoms present in the hydrocarbyl groups R^1 to R^{13} will tend to increase the melting point, although this effect can be
30 counteracted somewhat by asymmetry and branching, and the tendency of sterically bulky ions to coordinate poorly. For

example, steric bulk around the phosphorus atom or nitrogen atom of the cation or the sulfur atom or phosphorus atom of the anion will tend to decrease melting point of the salt and may be preferred. Therefore, more preferred are compounds wherein
5 each of R^9 , R^{10} , R^{11} , R^{12} , and R^{13} and one or more of R^1 , R^2 , R^3 , and R^4 or one or more of R^4 , R^5 , R^6 , R^7 , and R^8 has three or more carbon atoms. Also, branching of the hydrocarbyl groups R^1 to R^{13} tends to decrease the melting point of the compound. Branching can occur at the alpha or omega carbon or at any
10 intermediate point. In cases where the compound contains a phosphonium cation, the melting point tends to decrease as the degree of asymmetry around the phosphorus atom increases. For compounds containing an imidazolium cation, the melting melt will tend to decrease as the degree of symmetry in the
15 imidazolium cation decreases.

For example, tetrabutylphosphonium dibutylphosphate is a solid at room temperature, but tri(iso-butyl)(n-butyl)phosphonium dibutylphosphate is a liquid at room temperature, despite the fact that both compounds have 24
20 carbon atoms.

Notably, certain compounds of formula (I) may have melting points below room temperature, below 0°C and even below -20°C , in which case they may be suitable for use as solvents for reactions carried out at correspondingly low temperatures.
25 For example, tetrabutylphosphonium butylsulfate remains a liquid at -20°C .

Compounds according to formula (I) that are hydrophobic or "water immiscible" are preferred for some purposes. The term "water immiscible" is intended to describe
30 compounds that form a two phase system when mixed with water but does not exclude ionic liquids that dissolve in water nor ionic liquids that will dissolve water, provided that the two

phase system forms. Compounds that have a large total number of carbons, equal to or greater than 20 and in particular greater than 25 or 26, or have at least one aryl group are more hydrophobic. Water immiscibility is a desirable feature of an ionic liquid not only because it renders the compound useful for biphasic reactions with an aqueous phase, but also because it facilitates purification and isolation of the ionic liquid when prepared according to certain methods. There is no critical upper limit on the total number of carbon atoms that may be present in a compound of formula (I). However, it is unlikely that the total will exceed 50.

Thus, the current invention contemplates compounds of formula (I) where properties may be modified by varying the values of the R groups present on either the anion or the cation. Selection of particular values for R^1 to R^{13} to achieve particular melting points and degrees of water immiscibility is within the competence of a person skilled in the art, although it may require some routine experimentation.

Compounds according to formula (I) that have chirality provide a chiral environment for chemical reactions and may be especially preferred for certain purposes, such as a reaction having an asymmetric or chiral transition state that may be stabilized by interaction with a suitable solvent. Examples of chiral compounds of formula (I) include compounds containing a phosphonium cation wherein R^1 to R^4 are all different or one of R^1 to R^4 is an enantiomer, such as 2,4,4'-trimethylpentyl, which group has one chiral atom.

Examples of preferred compound according to formula (I) include:

tri-(n-butyl)methylphosphonium methylsulfate;
tri-(n-butyl)ethylphosphonium ethylsulfate;

tetra-(n-butyl)phosphonium n-butylsulfate;

triethyl-(n-butyl)phosphonium n-butylsulfate;

tetrabutylphosphonium dibutylphosphate;

tri-iso-butyl-butylphosphonium dibutylphosphate.

5 N,N-dimethylimidazolium dimethylphosphate;

N-methyl-N-butylimidazolium dibutylphosphate; and

N-methyl-N-ethylimidazolium ethylethanephosphonate;

and

tributylmethylphosphonium

10 methyltrifluoromethanephosphonate.

In general, a phosphonium or imidazolium salt of formula (I) can be prepared by reacting a compound of formula (II) or formula (III), respectively, with one of the following: (1) a sulfate diester of formula (IV); (2) a phosphate triester
15 of formula (V); or (3) a phosphonate diester of formula (VI).

In a preferred procedure for preparing compounds of formula (I), a tertiary phosphine of formula (II) or an imidazole of formula (III) is added directly to an ester (a sulfate diester, phosphate triester, or phosphonate diester),
20 with stirring. The reaction is suitably carried out at an elevated temperature, for example in the range of 140°C to 190°C, under an inert atmosphere.

The overall reaction is exothermic. Therefore, in order to control the temperature of the reaction mixture, it
25 may be desirable to control the rate of addition in some cases and perhaps also to apply external cooling during the addition step. Since alkylphosphines may be pyrophoric, the addition of trialkylphosphine should also be controlled in order to avoid

having a large amount of unreacted trialkylphosphine present in the reaction mixture, especially when the reaction is being carried out at elevated temperatures, for example over 100°C.

In general, the phosphine or imidazole and ester are present in the foregoing reaction in substantially stoichiometric amounts. In some cases, however, yields may be improved by using a slight molar excess of the phosphine or imidazole relative to the ester, for example in the range of 1.01 to 1.4 equivalents and preferably around 1.02 equivalents of the phosphine or imidazole.

Preferably, the reaction is carried out in the absence of solvent, in order to avoid a further step of purifying product away from solvent. However, the reaction may also be carried out in the presence of a solvent. In some cases, the presence of a solvent may be preferred as the solvent may enhance the rate at which the reaction proceeds.

The temperature of the reaction is not critical, although lower temperatures will result in longer reaction times. The reaction proceeds readily at elevated temperature, say up to 220°C, preferably in the range of 140-190°C, and is often complete in 8 hours at these temperatures. Certain alkylating agents, such as dimethyl-sulfate, are very active alkylating reagents and may be used for reactions carried out at room temperature. The initial step of adding the ester compound to the phosphine or imidazole, when required, may be conveniently carried out at room temperature.

The pressure of the reaction is not critical, and the reaction may be conveniently carried out at atmospheric pressure, preferably under an inert atmosphere, such as nitrogen. It is further preferable that the atmosphere be dry, in order to minimize the water content of the product.

If desired, any unreacted starting materials and/or residual water may be removed by, for example, drying under vacuum.

The foregoing process may be especially preferred if it is desirable to avoid contamination of end-product with halide ions or to avoid or minimize the amount of water contained in the end-product. However, compounds of formula (I) may be prepared by any suitable procedure.

The phosphonium and imidazolium salts of the current invention may be used as polar solvents for chemical reactions such as Michael additions, aryl coupling, Diels-Alder, alkylation, biphasic catalysis, Heck reactions, hydrogenation, or for enzymatic reactions, for example lipase reactions.

EXAMPLES:

In the following examples, starting material phosphines are made by Cytec Canada, Inc. and their purity determined by gas chromatography (GC). N-methylimidazole and dibutylsulfate were purchased from Lancaster. The remaining starting materials were purchased from Aldrich and used as they were purchased. Structures were confirmed by ^1H -NMR, ^{13}C -NMR and ^{31}P -NMR.

Example 1:

Preparation of tri-(n-butyl)methylphosphonium methylsulfate

To a flask containing 132 g (99% pure, 1.036 mole) dimethylsulfate, at room temperature, tri(n-butyl)phosphine (218 g, 98% pure, 1.056 mole) was gradually added, over a period of three hours, with stirring under nitrogen. The temperature in the flask increased gradually to 100°C during the addition.

When the addition was complete, the reaction mixture was heated to 150°C for 8 hours, then dried in a rotary evaporator under 140°C/5mm Hg for 5 hours.

Tri-(n-butyl)methylphosphonium methylsulfate product was obtained in 100% yield (348 g). NMR analysis was consistent with tri-(n-butyl)methylphosphonium methylsulfate. The product was a liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 3.46 (s, 3H, $-\text{OCH}_3$), 2.09 (m, 6H, $3 \times \text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-P}^+$), 1.71 (d, 3H, CH_3P^+), 1.32 (m, 12H, $3 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 0.76 (m, 9H, $3 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{P}^+$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 27.00 (P^+).

Example 2: tri-(n-butyl)ethylphosphonium ethylsulfate

To a flask containing 100 g (98% pure, 0.636 mole) diethylsulfate, at 60°C, tri(n-butyl)phosphine (132 g, 98% pure, 0.638 mole) was added gradually, over a period of two hours, with stirring under nitrogen. The temperature in the flask increased slowly to 120°C during the addition.

When the addition was complete, the reaction mixture was heated to 150°C for 3 hours, then dried in a rotary evaporator under 160°C/5mm Hg for 5 hours.

Tri-(n-butyl)ethylphosphonium ethylsulfate product was obtained in 100% yield (230 g). Analysis by NMR was consistent with tri-(n-butyl)ethylphosphonium ethylsulfate. The product was a liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 4.05 (q, 2H, $-\text{O-CH}_2\text{-CH}_3$), 2.34 (m, 6H, $3 \times \text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-P}^+$), 2.34 (m, 2H, $\text{CH}_3\text{-CH}_2\text{-P}^+$), 1.27 (m, 3H, $\text{CH}_3\text{-CH}_2\text{P}^+$), 1.27 (m, 3H, $-\text{OCH}_2\text{-CH}_3$), 0.97 (m, 9H, $3 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{P}^+$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 35.05 (s, P^+).

Example 3: tetra-(n-butyl)phosphonium butylsulfate

To a flask containing: 50 g (95% pure, 0.226 mole) di-(n-butyl)sulfate, at 80°C, tri(n-butyl)phosphine (48 g, 98% pure, 0.233 mole) was gradually added, over a period of one hour, with stirring under nitrogen. The temperature in the flask increased gradually to 120°C during the addition.

When the addition was complete, the reaction mixture was heated to 190°C for 8 hours, then dried in a rotary evaporator under 160°C/5mm Hg for 5 hours.

Tetra-(n-butyl)phosphonium n-butylsulfate product was obtained in 96% yield (90 g). Analysis by NMR was consistent with tetra-(n-butyl)phosphonium n-butylsulfate but indicated that the product contained some impurity. The product was a liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 3.77 (t, 2H, $-\text{OCH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.09 (m, 8H, $4 \times \text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2-\text{P}^+$), 1.41 (qu, 2H, $-\text{OCH}_2-\text{CH}_2-\text{CH}_2\text{CH}_3$), 1.33 (m, 16H, $4 \times \text{CH}_3-\text{CH}_2\text{CH}_2-\text{CH}_2\text{P}^+$), 1.19 (qu, 2H, $-\text{OCH}_2\text{CH}_2-\text{CH}_2-\text{CH}_3$), 0.76 (m, 12H, $4 \times \text{CH}_3-\text{CH}_2\text{CH}_2\text{CH}_2\text{P}^+$), 0.76 (m, 3H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-\text{CH}_3$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 33.49.

Example 4: synthesis of tri-ethyl(n-butyl)phosphonium butylsulfate

Triethylphosphine (7.2g, 99%, 0.06 mol) was added dropwise to a 125 mL flask containing 12.6 (99%, 0.06 mol) di-n-butylsulfate at 80°C under nitrogen and with stirring over a period of 75 minutes. The liquid was stirred at 140°C for an additional 3.5 hours. The liquid was cooled, moved to a rotary evaporator and dried at 125°C/5mm Hg for 6 hours. The product (16.73 g, yield 85%) was a wax-like solid at room temperature (m.p. from DSC measurement: 40.0°C). $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz,

δ): 3.98 (t, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-O-}$), 2.34 (m, 8H, $3 \times \text{CH}_3\text{-CH}_2\text{P}^+$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.54 (m, 8H, $\text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{O-}$ and $\text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.25 (m, $3 \times \text{CH}_3\text{-CH}_2\text{P}^+$), 0.91 (m, 6H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{O-}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 38.88 (s, P^+).

5 Example 5: synthesis of tetrabutylphosphonium dibutylphosphate

Tri-n-butylphosphine (215 g, 94%, 1.0 mole) was added dropwise over a period of 4 hours to a flask containing 272 g (98%, 1.0 mole) of tributylphosphate at 170°C. When the addition was complete, the reaction mixture was heated to 200°C and stirred at this temperature for 24 hours. The viscous liquid was dried in a rotary evaporator at 160°C/5 mm Hg for 5 hours. The product (363 g, yield 77.5%) was pure according to NMR. At room temperature the product was a white, wax-like solid (m.p. from DSC measurement: 28.0°C). $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 3.84 (q, 4H, $2 \times \text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{-O-}$), 2.38 (m, 8H, $4 \times \text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.53 (m, 16H, $4 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.40 (m, 8H, $2 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{O-}$), 0.97 (m, 12H, $4 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{P}^+$), 0.90 (m, 6H, $2 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{O-}$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 33.72 (P^+), 0.94 [m, $(\text{RO})_2\text{-P(=O)-O}^-$].

20 Example 6: synthesis of tri-iso-butyl-butylphosphonium dibutylphosphate

Tri-iso-butylphosphine (206.5 g, 98%, 1.0 mole) was added dropwise over a period of 2 hours to a flask containing 271.8 g (98%, 1.0 mole) of tributylphosphate at 200°C under nitrogen and stirring. When the addition was complete, the mixture was stirred at the same temperature for an additional 15 hours. The mixture was cooled down and moved to a rotary evaporator and dried under 160°C/5mm Hg for 5 hours. The product (320.7 g, yield 68.5%) was pure judged from NMR and liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 3.76

(q, 4H, $2 \times \text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{O-}$), 2.19 (q, 6H, $3 \times \text{CH}_3(\text{CH}_3)\text{CH-CH}_2\text{P}^+$), 1.96 (m, 3H, $3 \times \text{CH}_3(\text{CH}_3)\text{CH-CH}_2\text{P}^+$), 1.96 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.44 (m, 8H, $\text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{O-}$), 1.24 (m, 4H, $\text{CH}_3\text{-CH}_2\text{CH}_2\text{-CH}_2\text{P}^+$), 1.01 (d, 18H, $3 \times \text{CH}_3\text{CH}(\text{CH}_3)\text{-CH}_2\text{P}^+$), 0.84 (t, 3H, $\text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{P}^+$), 0.77 (t, 6H, $2 \times \text{CH}_3\text{-CH}_2\text{CH}_2\text{CH}_2\text{O-}$). ^{31}P -NMR (CDCl_3 , 81.015 MHz, δ): 32.60 (P^+), -0.61 [d, $(\text{RO})_2\text{-P(=O)-O}^-$].

Example 7: synthesis of N,N-dimethylimidazolium dimethylphosphate

Trimethylphosphate (127.6 g, 0.883 mole) was added dropwise over a period of 1 hour to a 300 ml flask containing 72.2 g (99%, 0.87 mole) N-methylimidazole at room temperature. The temperature of the reaction mixture was slowly increased to 140°C. As the reaction mixture approached 140°C, there was an acceleration in the rate at which the temperature increased. The reaction mixture was stirred at the same temperature for an additional 3 hours. The mixture was cooled and moved to a rotary evaporator and dried at 150°C/5mm Hg for 4 hours. The product (194 g, yield 100%) was pure, judged from NMR and liquid at room temperature. ^1H -NMR(CDCl_3 , 300.13 MHz, δ): 10.40 (s, 1H, $-\text{N-CH=N-}$), 7.43 (s, 2H, $-\text{N-CH=CH-N-}$), 3.91 (s, 6H, N- CH_3), 3.46 (d, 6H, $-\text{OCH}_3$). ^{31}P -NMR (CDCl_3 , 81.015 MHz, δ): 3.01 [s, $(\text{RO})_2\text{-P(=O)-O}^-$].

Example 8: synthesis of N-methyl-N-butylimidazolium dibutylphosphate

Tributylphosphate (137.2 g, 0.505 mole) was added dropwise, slowly, to a 300 ml flask containing 41.5 g (99%, 0.5 mole) N-methylimidazole at 170°C under nitrogen and stirring. The liquid was stirred at the same temperature for an additional 5 hours. The liquid was cooled and moved to a rotary evaporator and dried at 150°C/5mm Hg for 4 hours. The

product (171.3 g, yield 98%) was pure, as judged from NMR, and was liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 10.37 (s, 1H, $-\text{N-CH=N-}$), 7.50 (s, 1H, $-\text{N-CH=CH-N-}$), 7.29 (s, 1H, $-\text{N-CH=CH-N-}$), 4.09 (t, 2H, $-\text{N-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_3$), 3.87 (s, 3H, $-\text{N-CH}_3$), 3.67 (m, 4H, $-\text{O-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_3$), 1.67 (qu, 2H, $-\text{NCH}_2\text{-CH}_2\text{-CH}_2\text{CH}_3$), 1.40 (m, 4H, $2 \times -\text{OCH}_2\text{-CH}_2\text{-CH}_2\text{CH}_3$), 1.16 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{-CH}_2\text{-CH}_3$), 1.16 (m, 2H, $-\text{NCH}_2\text{CH}_2\text{-CH}_2\text{-CH}_3$), 0.70 (m, 6H, $2 \times -\text{OCH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$), 0.70 (m, 3H, $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 0.95 [s, $(\text{RO})_2\text{-P(=O)-O}^-$].

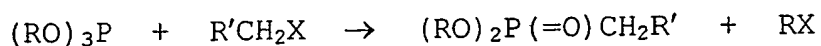
10 Example 9: synthesis of N-methyl-N-ethylimidazolium ethylethanephosphonate

Diethylethanephosphonate (68.2 g, 99%, 0.406 mole) was dripped into a 300 ml flask containing 33.3 g (99%, 0.402 mole) N-methylimidazole at 160°C under nitrogen and stirring over a period of 80 minutes. The liquid was stirred at the same temperature for an additional 10 hours. The liquid was cooled, moved to a rotary evaporator and dried at 140°C/5mmHg for 2.5 hours. The product (92.4 g, yield 92%) was a liquid at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300.13 MHz, δ): 10.99 (s, 1H, $-\text{N-CH=N-}$), 7.73 (s, 1H, $-\text{N-CH=CH-N-}$), 7.65 (s, 1H, $-\text{N-CH=CH-N-}$), 4.39 (q, 2H, $-\text{N-CH}_2\text{-CH}_3$), 4.09 (s, 3H, $-\text{NCH}_3$), 3.92 (m, 2H, $-\text{O-CH}_2\text{-CH}_3$), 1.56 (m, 3H, $-\text{OCH}_2\text{-CH}_3$), 1.56 (m, 2H, $-(\text{O=})\text{P-CH}_2\text{-CH}_3$), 1.19 (m, 3H, $-(\text{O=})\text{PCH}_2\text{-CH}_3$), 1.19 (m, 3H, $-\text{NCH}_2\text{-CH}_3$). $^{31}\text{P-NMR}$ (CDCl_3 , 81.015 MHz, δ): 25.57 [s, RO-(R)P(=O)-O^-].

25 Example 10: tetraalkylphosphonium alkyl alkanephosphonate

Tetraalkylphosphonium alkyl alkanephosphonate compounds can be made by reacting a trialkylphosphine with a dialkyl alkanephosphonate according to the process described in Example 1 except that dialkyl alkane phosphonate is used in place of dimethylsulfate.

Dialkyl alkanephosphonates which are used as starting materials can be made according to the Michaelis-Arbuzov reaction:



5 Typical Michaelis-Arbuzov reactions and conditions for carrying out the reactions are described in a review article by A. K. Bhattacharya, G. Thyagarajan, *Chemical Review*, 1981, volume 81, page 415 the contents of which are herein incorporated by reference. Michaelis-Arbuzov reactions
10 specifically for making dialkyl fluorinated alkanephosphonates, as exemplified by the synthesis of diethyl trifluoromethanephosphonate, are described in: T. Mahmood, J. M. Shreeve, *Synthesis Communications*, 1987, 17(1), 71-75, (the contents of which are herein incorporated by reference) and in
15 D. J. Burton, R. M. Flynn, *Synthesis*, 1979, 615. In addition, V. I. Shibaev, A. V. Garabadzhiu, A. A. Rodin, *Zh. Obshch. Khim.* 1983, 53(8), 1743-1745 (the contents of which are herein incorporated by reference) describes a method for synthesizing di(isobutyl) trifluoromethanephosphonate.

20 By way of illustration, in a typical reaction, one equivalence of the alkylhalide $R'CH_2X$ is added slowly into a flask containing 1.3-2 equivalence of trialkylphosphite $(RO)_3P$ through an addition funnel under stirring. The excess of the trialkylphosphite can serve as solvent for the reaction. The
25 reaction may be carried out over a range of temperatures, for example in the range of room temperature to 150°C. Preferably, the reaction is carried out at a temperature below the boiling points of the starting materials. The boiling point of trimethylphosphite is 112°C, triethylphosphite is 155°C. If an
30 elevated reaction temperature is preferred, the trialkylphosphite in the flask can be preheated to that temperature. After all material has been added the flask, the

reaction mixture can be refluxed for a suitable period of time, typically several hours. Any remaining unreacted trialkylphosphite and the byproduct alkylhalide $R'X$ of the reaction can be removed by evaporating the mixture under

5 vacuum.

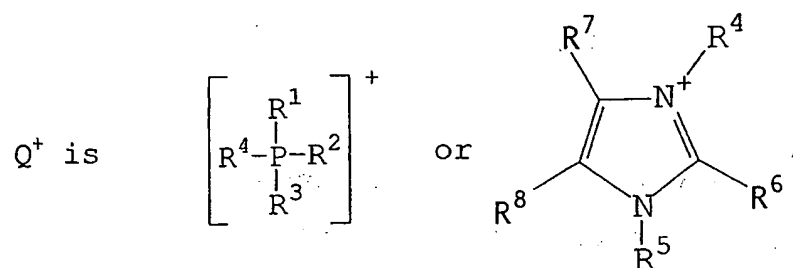
The foregoing reaction may be used to make partially and completely fluorinated alkane phosphonates for use in making salts of formula (I). For example, when a compound represented by the general formulae $C_nF_{2n+1}I$ is used as the alkyl
10 halide in the foregoing reaction, the resulting Michaelis-Arbuzov phosphonate is a dialkyl perfluoroalkanephosphonate. When reacted with a trialkylphosphine, the resulting phosphonium salt is a tetraalkylphosphonium alkyl
15 perfluoroalkanephosphonate, which compounds may be especially preferred for some applications, such as two-phase reactions where one phase is aqueous and the ionic liquid phase is necessarily hydrophobic.

CLAIMS:

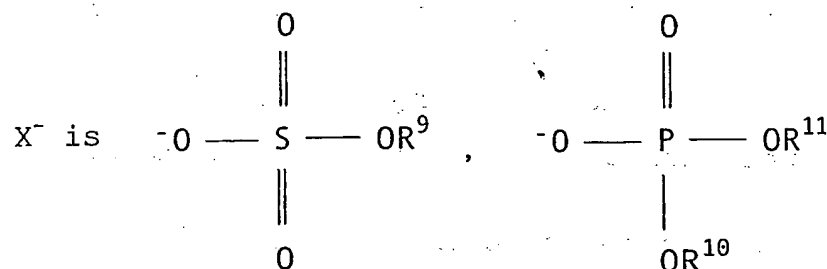
1. A compound having the general formula (I):



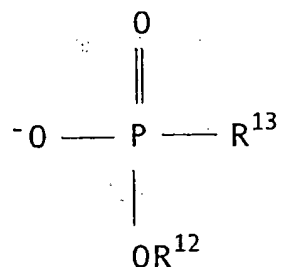
wherein



and



or



- 15 and wherein:

each of R^1 , R^2 , R^3 , R^4 , R^5 , R^9 , R^{11} , R^{12} and R^{13} is independently a hydrocarbyl group;

each of R^6 , R^7 and R^8 is independently a hydrogen or a hydrocarbyl group;

- 20 with the proviso that:

(i) when Q^+ is a phosphonium cation and X^- is a phosphate, or a phosphonate anion other than a phosphonate in

which R^{13} is perfluorohydrocarbyl, then R^1 , R^2 , R^3 , and R^4 each has three or more carbon atoms;

(ii) when Q^+ is a phosphonium cation and X^- is a sulfate then the sum of carbon atoms in R^1 , R^2 , R^3 , and R^4 is greater than 4;

(iii) when Q^+ is an imidazolium cation, X^- is not a sulfate anion; and

(iv) when Q^+ is a phosphonium cation, X^- is methylsulfate, and one of R^1 , R^2 , R^3 , and R^4 is methyl, the others of R^1 , R^2 , R^3 , and R^4 cannot be 2-cyanoethyl.

2. A compound according to claim 1, wherein Q^+ is a tetralkylphosphonium and X^- is an alkylsulfate anion.

3. A compound according to claim 2, wherein R^1 , R^2 , and R^3 are hydrocarbyl groups with three or more carbon atoms.

4. A compound according to claim 2, wherein R^1 , R^2 , and R^3 are each n-butyl.

5. A compound according to any one of claims 2 to 4, wherein:

(a) R^4 is methyl and R^6 is methyl; or

(b) R^4 is ethyl and R^6 is ethyl; or

(c) R^4 is n-butyl and R^6 is n-butyl.

6. A compound according to claim 1, wherein the compound is selected from the group consisting of

tri-(n-butyl)methylphosphonium methylsulfate;

tri-(n-butyl)ethylphosphonium ethylsulfate;

tetra-(n-butyl)phosphonium n-butylsulfate;

triethyl-(n-butyl)phosphonium n-butylsulfate;

tetrabutylphosphonium dibutylphosphate;

tri-iso-butyl-butylphosphonium dibutylphosphate

N,N-dimethylimidazolium dimethylphosphate;

5 N-methyl-N-butylimidazolium dibutylphosphate; and

N-methyl-N-ethylimidazolium ethylethanephosphonate;

and

tributylmethylphosphonium

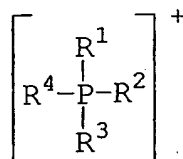
methyltrifluoromethanephosphonate.

10 7. A process for preparing a compound of formula (I):

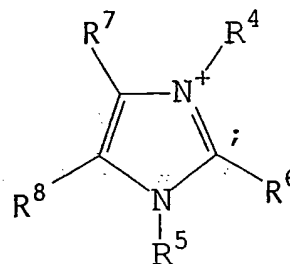


wherein

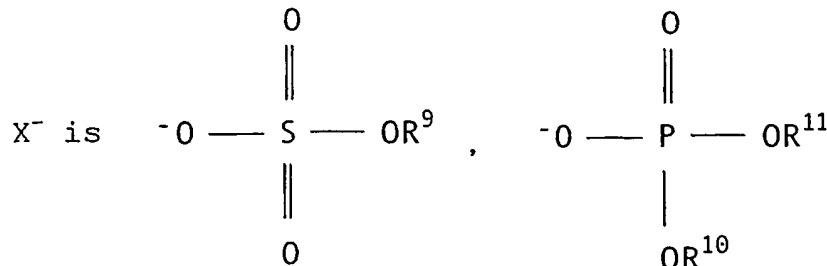
15 Q^+ is



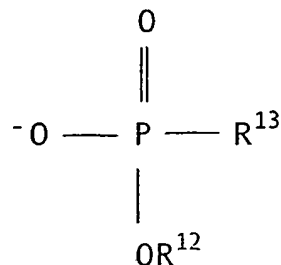
or



and



or



and wherein:

each of R^1 , R^2 , R^3 , R^4 , R^5 , R^9 , R^{10} , R^{11} , R^{12} , and R^{13} is independently a hydrocarbyl group;

each of R^6 , R^7 , and R^8 , is a hydrogen or hydrocarbyl
5 group;

with the provisoes that:

(i) when Q^+ is a phosphonium cation and X^- is a phosphate, or a phosphonate anion other than a phosphonate in which R^{13} is perfluorohydrocarbyl, then R^1 , R^2 , R^3 , and R^4 each
10 has three or more carbon atoms;

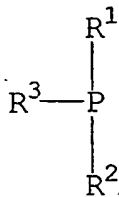
(ii) when Q^+ is a phosphonium cation and X^- is a sulfate then the sum of carbon atoms in R^1 , R^2 , R^3 , and R^4 is greater than 4;

(iii) when Q^+ is an imidazolium cation, X^- is not a
15 sulfate; and

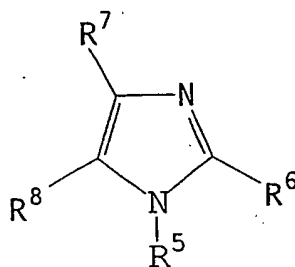
(iv) when Q^+ is a phosphonium cation, X^- is methylsulfate, and one of R^1 , R^2 , R^3 , and R^4 is methyl, the others of R^1 , R^2 , R^3 , and R^4 cannot be 2-cyanoethyl.

the process comprising reacting a compound of formula (II):

20

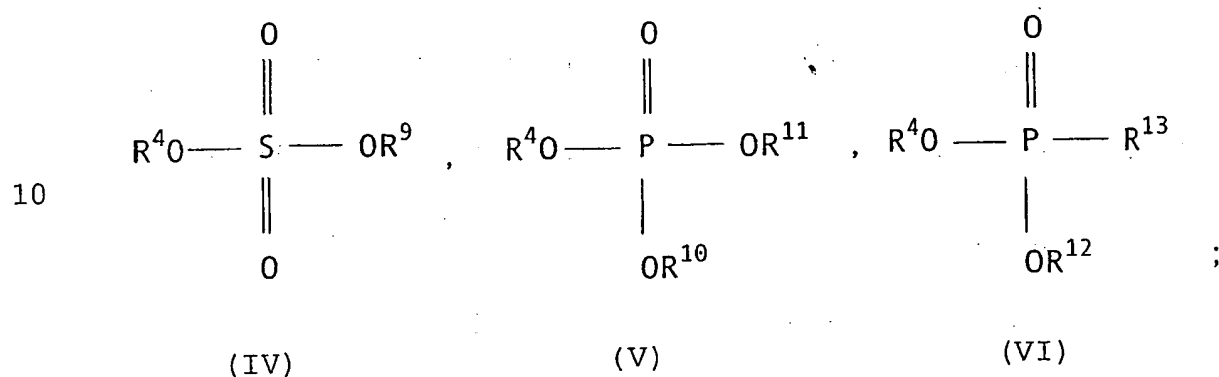


wherein each of R^1 , R^2 , and R^3 is independently a hydrocarbyl group, or formula (III):



5 wherein R^5 is a hydrocarbyl group, and cation of R^6 , R^7 and R^8 is independently a hydrogen or hydrocarbyl group,

with a compound defined by one of the following formulae:



wherein each of R^4 , R^9 , R^{10} , R^{11} , R^{12} and R^{13} is a hydrocarbyl group.

15 8. The process of claim 7, wherein the reaction is carried out in the absence of solvent.

9. The process of claim 7, wherein Q^+ is a tetralkylphosphonium and X^- is an alkylsulfate anion.

10. The process of claim 9, wherein R^1 , R^2 , and R^3 are
20 hydrocarbyl groups with three or more carbon atoms.

11. The process of claim 9, wherein R^1 , R^2 , and R^3 are each n-butyl.

12. The process of any one of claims 7 to 11, wherein

(a) R^4 and R^6 are both methyl; or

(b) R^4 and R^6 are both ethyl; or

(c) R^4 and R^6 are both n-butyl.

13. The process of claim 7 or 8, wherein the compound of formula (I) is selected from the group consisting of

5 tri-(n-butyl)methylphosphonium methylsulfate;

tri-(n-butyl)ethylphosphonium ethylsulfate;

tetra-(n-butyl)phosphonium n-butylsulfate;

triethyl-(n-butyl)phosphonium n-butylsulfate;

tetrabutylphosphonium dibutylphosphate;

10 tri-iso-butyl-butylphosphonium dibutylphosphate

N,N-dimethylimidazolium dimethylphosphate;

N-methyl-N-butylimidazolium dibutylphosphate; and

N-methyl-N-ethylimidazolium ethylethanephosphonate;

and

15 tributylmethylphosphonium
methyltrifluoromethanephosphonate.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F9/54 C07D233/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 01 87900 A (ROBERTSON ALLAN JAMES ; CYTEC TECH CORP (US)) 22 November 2001 (2001-11-22) claims 1-14	1-13
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 December 2003

Date of mailing of the international search report

02/01/2004

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Kyriakakou, G

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 1 182 197 A (SOLVENT INNOVATION GMBH) 27 February 2002 (2002-02-27) claims 1-12 ---	1-13
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